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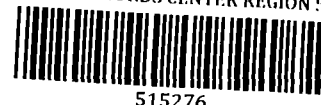*Project Summary*

Evaluation of the Effectiveness of Granular Activated Carbon Adsorption and Aquaculture for Removing Toxic Compounds From Treated Petroleum Refinery Effuents

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The effectiveness of granular activated carbon for removal of selected priority pollutants from petroleum refinery wastewaters was evaluated under both laboratory and field conditions. The effectiveness of aquaculture was evaluated under field conditions.

Activated carbon adsorption isotherms of prepared aqueous solutions of toluene, 2,4-dimethylphenol, naphthalene, benzo(a)pyrene, chrysene, pyrene, acenapthene, phenanthrene, fluoranthene, and fluorene were determined by laboratory studies to estimate the optimum loading capacity under ideal conditions. The adsorption capacity and loading capacity of the pulverized activated carbon for the specific organic compounds were calculated with the Freundlich equation.

Effectiveness of activated carbon and aquaculture for removal of organic compounds from a treated petroleum refinery wastewater was evaluated with a pilot-scale treatment system onsite at a refinery. Comparison of effluent quality from the activated carbon columns versus conventional biological treatment in aerated lagoons as measured by chemical criteria and continuous flow bioassays showed the activated carbon to be effective in removing organic compounds and re-ducing toxicity of the wastewater. A pilot-scale aquaculture treatment system was also shown to be effective in reducing toxicity of the treated wastewater.

A literature review of activated carbon treatment indicated considerable variation in estimates for both capital investments and annual operating costs. Capital investment costs for granular activated carbon facilities· ranged from $540,000 - $2,300,000 (1970) to $587,000 - $3,175,000 (1978) for plants from 1 to 20 million gallons per day. Annual operating costs for granular activated carbon systems varied from 4.8¢ to 40¢ per 1,000 gallons of water treated depending upon type of wastewater and amount of pretreatment.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Because of the intensified interest in the removal of toxic pollutants from petroleum refinery effluents, an evaluation of the effectiveness of treatment schemes necessary to accomplish this

removal is required. Activated carbon is well known as a good adsorbent for removal of organic compounds from aqueous solutions and has been proposed as a relatively efficient method for removing organics from refinery wastewaters. Aquaculture is a potential inexpensive mode of treatment for removal of dilute concentrations of toxic pollutants.

Under the sponsorship of the U.S. Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory, the effectiveness of activated carbon for removal of selected priority pollutants from petroleum refinery effluents was evaluated under both laboratory and field conditions. The effectiveness of aquaculture in removing toxic compounds from treated refinery effluents was evaluated under field conditions.

Adsorption isotherms of prepared aqueous solutions were determined for 10 specific priority pollutants identified in the 1976-1977 EPA survey of petroleum refinery wastewaters: toluene, 2,4-dimethylphenol, naphthalene, benzo(a)pyrene, chrysene, pyrene, acenapthene, phenanthrene, fluoranthene, and fluorene.

In addition, effectiveness of activated carbon for removal of toxic compounds from a petroleum refinery wastewater was evaluated with a pilot-scale treatment system onsite at a refinery. The criterion for determining the effectiveness of removal was toxicity reduction as measured by continuous flow bioassays. A comparison of the effluent quality from three modes of treatment—conventional biological, dual-media filtration-activated carbon (DM-AC), and pilot-scale aquaculture—was made based on chemical measurements and continuous-flow bioassay results.

The final objective of this project was to review the literature on the cost of activated carbon adsorption as a treatment mode for removing organic compounds from petroleum refinery wastewaters.

Process

Adsorption Isotherms

Aqueous solutions of the specific chemical compounds were prepared, and isotherm tests (using pulverized granular activated carbon) were conducted for each compound. The quantity of 2,4-dimethylphenol and toluene remaining in aqueous solutions after contact with the carbon was analyzed with a total organic carbon instrument. The concentration of naphthalene, benzo(a)pyrene, chrysene, pyrene, acenapthene, phenanthrene, fluoranthene, and fluorene was determined using a Fluorescent Spectrophotometer. Data were analyzed by the Freundlich equation:

$$\frac{x}{m} = KC_f^{1/n}$$

where:

x = quantity of solute adsorbed in mg
m = weight of carbon in g
K = intercept at $C_f = 1$
C_f = final quantity of solute in mg
$1/n$ = slope of the line.

Onsite Evaluations

A pilot-scale DM-AC treatment system mounted in a mobile trailer was located onsite at an oil refinery. The dual-media filter column was filled sequentially with pea-sized gravel (10 cm), #1220 garnet sand (35 cm), and #2 anthracite coal. The filtration column was designed for downflow gravity filtration with valving for hydraulic backflushing.

Following filtration, the system was designed for sequential flow through a series of four activated carbon columns. Each column was filled with approximately 13.5 kg (152 cm in column) of granular activated carbon. Carbon was changed prior to exceeding a loading capacity of 1 g of COD per 10 g of carbon.

A pilot-scale aquaculture treatment system was constructed onsite at the refinery. The major components of the aquaculture system consisted of a sequential series of six pools. Each pool was 5.48 m in diameter and 1.2 m in depth. The first three pools in the series were operated for optimum growth of algae. The fourth pool was stocked with 2,898 kg/ha of mussels and 951 kg/ha of *Tilapia Aurea*. The fifth pool was stocked with 7,730 kg/ha of mussels and 2,183 kg/ha of *Tilapia*. The sixth pool was stocked with 2,319 kg/ha of mussels, 2,533 kg/ha of *Tilapia*, and 0.93 m² of the emergent plant, Primrose Willow (*Jussiaea diffusa*). Flow rate of the wastewater through the aquaculture system was maintained at 3 to 4 liters per minute for an estimated retention time of 3.7 to 5 days per pool.

Influent water to the pilot-scale aquaculture and DM-AC treatment systems was pumped from the point of final discharge from the oil refinery treatment system. The refinery treatment system consisted of sequential treatment with a primary API separator, dissolved air flotation unit, aerated lagoon, and waste stabilization lagoons. Water from each of the test units passed through duplicate artificial streams for performance of continuous-flow bioassays using benthic macroinvertebrates and fish. Assemblages of macroinvertebrates were collected from a natural stream using Hester-Dendy samplers. Nine of these samplers were placed in each artificial stream. Ten caged fathead minnows were also placed in each artificial stream.

Results

Nine of the ten compounds tested showed a good positive correlation with the Freundlich equation (Table 1). Adsorption data for benzo(a)pyrene (BAP) did not fit the Freundlich equation but did show a high correlation with a normal arithmetic linear regression equation when the dose of carbon was plotted against the quantity of BAP adsorbed. Apparently the sorption mechanism for BAP was different from the other compounds.

Except for toluene, the adsorption capacity appeared to decrease with respect to an increase in complexity of the polynuclear aromatic molecule. Although toluene data showed an excellent fit with the Freundlich equation, the actual loading factor for toluene appears to be lower than would be predicted for the physical-chemical properties of the compound.

The adsorption isotherm data indicate that activated carbon could be used to remove polynuclear aromatic hydrocarbon compounds from aqueous wastes. However, relatively high dosages of carbon would be required to remove the five-membered aromatic ring compounds such as chrysene and BAP. For example, it would require 1,667 mg/l of activated carbon to reduce the concentration of chrysene from 0.01 mg/l to 0.001 mg/l in a single-stage contactor, calculated from the Freundlich equation.

Onsite Evaluations

The final effluent from the aerated lagoon treatment system at this refinery was of good quality with respect to the chemical criteria specified in the NPDES effluent guidelines.

The total cumulative mortality of fathead minnows exposed to the normal lagoon effluent was 25 percent (Table 2). In contrast, no mortality was observed during the 32-day exposure of the fish to either of the pilot-scale advanced treatment systems.

The number of species of benthic macroinvertebrate organisms was higher after exposure to the two pilot-scale treatment system than that of the aerated lagoon effluents (Table 3). Also,

the mean density of individuals of macroinvertebrate organisms exposed to the pilot system effluents was over 100 percent higher than that of the aerated lagoon effluent.

The DM-AC treatment system reduced the BOD₅, COD, TOC, and TSS concentrations of the aerated lagoon effluent by approximately 50, 75, 75, and 60 percent, respectively (Table 4). There were no significant differences in concentrations of nitrate-nitrogen and total phos-

phate-phosphorus. The aquaculture system reduced the BOD₅, nitrate, phosphate, and TSS concentrations by approximately 60, 90, 55, and 60 percent, respectively. There were no significant differences in COD and TOC concentrations.

Economics

A literature review of activated carbon treatment indicates considerable variation in estimates of both capital investments and annual operating costs. Estimation of treatment costs is difficult, since each system reacts differently. Comparison of design criteria is also difficult, since systems may have different design parameters. Capital investment costs for 1 to 20 million gallons per day (MGD) granular activated carbon treatment facilities ranged from $540,000 to $2,300,000 (1970) to $587,000 to $3,175,000 (1978). Estimated capital investment costs for powdered activated carbon treatment systems of 2 to 20 MGD capacity ranged from $406,000 to $912,000 with regeneration capabilities and $123,000 to $1,050,000 without regeneration capabilities.

Annual operating costs for granular activated carbon systems varied from 4.8¢ to 40¢ per 1,000 gallons of water treated, depending upon the type of wastewater and the amount of pretreatment. Operating costs for powdered carbon systems varied from 1.5¢ to 7.0¢ per 1,000 gallons treated, depending on influent flow and quality.

Conclusions

Activated carbon was shown to be effective in removing selected organic compounds from petroleum refinery wastewaters; however, there was a wide variation in the adsorption capacities of the 10 compounds tested. In general, adsorption capacity of activated carbon appears to decrease with an increase in the complexity of the poly-nuclear aromatic molecule; therefore, it would require relatively high dosages of carbon to remove the five-membered aromatic ring compounds such as chrysene and benzo(a)pyrene. As calculated from the Freundlich isotherm, it would require 1,667 mg/l of activated carbon to reduce the concentration of chrysene from 0.01 mg/l to 0.001 mg/l in a single-stage contactor.

Advanced treatment using activated carbon or aquaculture appears to significantly improve petroleum refinery wastewater with respect to toxicity

Table 1. Summary of Freundlich Parameters

Compound	$K^{(a)}$	$1/n$	r
Fluorene	196	0.57	0.95
2,4 dimethylphenol	184	0.09	0.93
Acenaphthene	140	0.43	0.97
Phenanthrene	135	0.45	0.89
Naphthalene	123	0.41	0.99
Fluoranthene	88	0.38	0.82
Pyrene	66	0.24	0.92
Toluene	40	0.35	0.93
Chrysene	6	0.50	0.82
Benzo(a)pyrene	(b)	(b)	-0.55

(a) K at $C_o = mg/l$.
(b) data did not fit Freundlich Equation, as indicated by low correlation coefficient.
r = correlation coefficient.

Table 2. Percent Mortality of Fathead Minnows (Pimephales Promelas)

	Treatment System		
	Aerated lagoon	Aquaculture	DM-AC
Days of Exposure	Percent mortality of replicates		
9/18/78 Start	0	0	0
8	0	0	0
11	0	0	0
16	10	0	0
22	5	0	0
24	0	0	0
29	5	0	0
32	5	0	0
Total Cumulative Mortality	25	0	0

Table 3. Response of Benthic Macroinvertebrate Organisms to Selectively Treated Oil Refinery Wastewater

	Number of species			Mean density[a]		
Days of Exposure	Aerated lagoon	Aquaculture	DM-AC	Aerated lagoon	Aquaculture	DM-AC
9/18/78 Start	44	44	44	2243	2243	2243
8	38	35	44	2985	1804	3868
16	39	40	41	5219	5262	6226
32	22	39	36	4689	10113	12352

[a]Number of organisms/m².

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reduction. There were no fathead minnow mortalities in either effluent during the 32-day study. In addition, the variety and abundance of benthic macroinvertebrates increased in the effluents of both pilot-scale advanced treatment systems.

Table 4. Mean Chemical Measurements for Selectively Treated Petroleum Refinery Effluents

Chemical Parameter	Mean concentration (mg/l)		
	Aerated lagoon	Aquaculture	DM-AC
BOD$_5$	20.2	8.1	9.9
COD	128.1	137.0	31.4
TOC	45.1	46.9	11.2
TSS	33.0	19.0	18.0
Nitrate-Nitrogen	3.65	0.45	3.87
Total Phosphate-Phosphorus	0.22	0.10	0.19

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